CHAPTER TWO: LITERATURE REVIEW

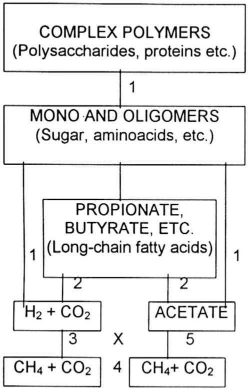
2.1 Mechanism of the Anaerobic Digestion Process

It was just a century ago when the anaerobic treatment was reported to be a useful method for the treatment of wastewaters (McCarty,1981). Many improvements have been made since then in both fundamental and practical aspects. Interest on anaerobic digestion in anaerobic treatment increased considerably because of the by-product methane which can serve as a fuel to help offset growing demand of energy. Recognition of the advantages of anaerobic treatment has resulted in broadening of application and use of anaerobic treatment processes throughout the world (Sastry and Vickineswary, 1995).

The anaerobic digestion process is a complex process in which several groups of facultative and anaerobic microorganisms, mainly bacteria, breakdown the organic waste materials to methane and carbon dioxide in the absence of molecular oxygen (Murk *et al.*, 1980). The process is widely used for the purification of wastes containing a high concentration of biodegradable organics. The mechanism of the anaerobic process is more complex than that of the aerobic process. According to the present knowledge, the complete degradation of complex organic matter to methane and carbon dioxide is found to proceed according to the multi step scheme shown in *Figure 2*.

Insoluble organic materials such as polysaccharides, proteins, and lipids are hydrolyzed to soluble units, such as oligosaccharides and sugars, peptides and amino acids and free fatty acids. This process is effected by the fermentative bacteria (Group 1) which then ferment these soluble substrates mainly to a mixture of organic acids, hydrogen, and CO_2 . Fatty acids with longer chain than acetate, as well as some other organic acids and alcohols, are converted to acetate, hydrogen and CO_2 by the hydrogen-producing (proton-reducing) acetogenic bacteria (Group 2). Many of these reactions are not thermodynamically favorable unless the partial pressure of hydrogen is maintained below 10^{-3} atmosphere by hydrogen-consuming organisms such as hydrogenotrophic methanogens (Wolin and Miller, 1992).

The net effect of these two groups is to convert complex organic matter to the primary substrates for methanogenesis, H_2 - CO_2, which is consumed by the hydrogenotrophic methanogens (Group 3), and acetate, which is split to CH_4 and CO_2 by the acetotrophic methanogens (Group 5). The importance of acetogenesis from H_2-CO_2 (Group 4, the hydrogen-consuming acetogens) has not been extensively studied (Zinder, 1988).



Legend:

1 : Fermentative bacteria

2 : Acetogenic bacteria

3 : Hydrogenotrophic methanogens

4 : Hydrogen consuming acetogens

5 : Acetotrophic methanogens

Figure 2. Flow of Carbon to Methane in a Typical Anaerobic Reactor (Zinder, 1988)

2.2 Historical Development of Anaerobic Treatment of Wastewater

It is well known over centuries that flammable marsh gas is produced by decomposition of organic matter under anaerobic conditions (Sastry, 1986). The earliest scientific investigation of this natural phenomenon was undertaken by Volta (1886) who demonstrated that the combustible air liberated by stirring marshy pools could be collected and used. He was the first to relate the decay of organic matter with the production of biogas. Biogas from a carefully designed septic tank was used for street lighting in Exeter, England in 1895 (Sastry, 1986).

The experience must have been successful enough to encourage others, as in the 1920s, to build several devices for the purpose of generating this gas, which is primarily methane. The process has also been used where energy supplies have been reduced as in France, Algeria and Germany during and after the second world war, when the methane thus produced was used to run automobiles (Sohngen, 1910).

At the turn of this century, in a preliminary study, Sohngen (1910) described the digestion of the salts of the fatty acids by enriched microbial cultures in the absence of oxygen, producing methane and carbon dioxide as the main final products.He found that other organic compounds can also be digested and that hydrogen gas is used by the anaerobic bacteria to convert carbon dioxide to methane. This reaction was also studied in detail by Schnellen (1906). Goenwege (1920) applied the fundamental microbiological research of Sohngen (1910) to the anaerobic digestion process for the treatment of wastewater. He considered the conversion of more complicated organic molecules to organic acids and alcohols as the first stage of the anaerobic purification process and stated that in the second stage, these products are converted to methane. In addition, he speculated that the slow growth of methane producing bacteria could cause the slow start-up of the septic tanks.

Slightly more than two decades ago as a result of rapid escalation in the energy costs, interest in the anaerobic digestion technology has expanded considerably because the process is of lower cost compared to the aerobic process as it requires no aeration. In addition, the methane produced from the process can serve as a useful fuel. The anaerobic digestion process has a lower sludge production rate, thereby minimizing the sludge disposal problem .

The principal disadvantage of the anaerobic process is the relatively low conversion of organic matter into biomass which makes it vulnerable to shock loadings (Dennis and Jennet, 1975). But, it should be realized that decreased cellular synthesis is also an advantage as the ultimate aim of the waste stabilization is the removal of organic matter and not the production of biomass. This is taken care of by using fixed film or the immobilized whole cell reactors.

The earliest full scale application of anaerobic digestion to industrial wastes was by Buswell and LeBosquet (1936) for treatment of distillery and dairy wastewaters. Buswell (1956) observed that the process is economical for treating wastewaters having 1-3% of digestible solids. Wastewaters with less than 1% solids are likely to result in an undesirably large installations. Such views are loosing validity as anaerobic digestion is being applied to treat an ever increasing variety of soluble organic industrial wastewaters.

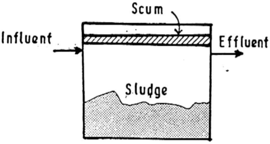
Subsequent developments over the years have led to some commonly accepted criteria that govern the successful and economical operation of anaerobic digestion systems. Some of these are (a) initial BOD above 1,000 mg/L, (b) nitrogen : BOD ratio of at least 2.5 : 100, (c) buffer capacity in relation to organic substances that form volatile acids, (d) low sulphur and settleable solids content and (e) neutral pH range and absence of toxic materials (Sastry and Mohan Rao, 1963; Sastry, 1985).

Anaerobic digestion of soluble organic wastewaters can be accomplished within a short duration and has been done with materials such as yeast wastewaters in 1.5 days (Rudolfs and Trubnick, 1949) and chewing gum wastewaters in 5 days (Logan and Rudolfs, 1947).

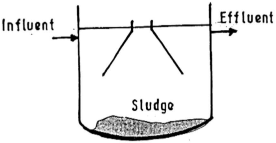
Anaerobic digestion has so far been applied to meat packing, milk, yeast, distillery, wood scouring, starch, rice, candy, pea-blancher, straw board, citrus, pharmaceuticals including antibiotics, tannery, synthetic drugs, sugars, tapioca and sago mill wastewaters, etc. Fullscale treatment plants of some of the above wastewaters are in operation in different parts of the world (Sastry and Mohan Rao, 1963).

In recent times, several designs of anaerobic reactors had been developed (*Figure* 3). However, due to several reasons such as lack of stability, low loading rates, slow recovery after failure and specific requirements for wastewater composition (Van Den Berg and Kennedy, 1983), this process was less widely used for treatment of industrial wastewater. Many improvements have been made since then in anaerobic digestion.

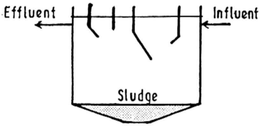
Since the problem in the anaerobic digestion process is often related to the loss of useful microorganisms to degrade the organic matter due to wash-out, extensive research has been carried out to increase the biomass density in the anaerobic reactors. Two types of mechanisms have been adopted for this purpose:



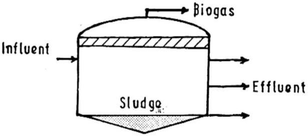
3a. Septic Tank



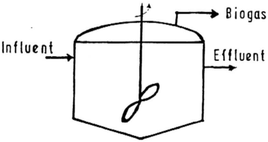
3b. Travis Tank



3c. Imhoff Tank



3d. Unstirred Reactor



3e. Stirred Reactor

Figure 3. Conventional Anaerobic Reactors

i) Providing conditions within the reactor which enhance the natural tendency of biomass to form aggregates which are large enough to separate from wastewater by settling.

ii) Providing surface within the reactor to which bacteria can attach in film. In this case carrier materials for bacteria are required.

Based on these two mechanisms, several new designs of anaerobic reactors have been developed such as the anaerobic contact reactor, clarigester, downflow stationary fixed film (DSFF) reactor, fluidized and expanded bed reactor, upflow anaerobic sludge blanket (UASB) reactor and the upflow anaerobic contact filter. The chronological development in anaerobic digestion is shown in *Table 3*.

Selection of the appropriate process configuration is critical to successful operation and requires detailed consideration. Different configurations give different ratio of solids retention time (SRT) and hydraulic retention time (HRT). Maximal SRT is desirable for process stability and minimal sludge production. Various types of reactor configurations have been used in anaerobic treatment of wastewaters. The most advanced processes with respect to anaerobic treatment are the fixed-film processes which use microbial films as a means of achieving high mean residence time thereby achieving highly cost-effective designs.

Table 3. Chronology of Development in Anaerobic Digestion (Sastry & Vickineswary, 1995)

Chronology of Development by Year	Important Milestone
1881	Mouras's automatic scavenger Suspended organic materials liquified in air tight chamber
1890	First use of upflow anaerobic filter in absence of air
1895	Development of septic tank
1897	Waste disposal tank at leper colony equipped with gas collectors
1904	Travis tank: suspended solids separated and passed into hydrolyzing chamber
1905	Imhoff tank: sludge retained in a separate chamber for several months and disposed without nuisance
1930	Importance of seeding and pH control in operation of anaerobic system
1950	Anaerobic clarigester with settling tank for return of sludge
1972	Development of anaerobic filter
1979	Development of upflow anaerobic sludge blanket process
1980	Development of anaerobic attached film expanded bed reactor

Biomass retention in the form of films allows operation of anaerobic processes at exceedingly low HRT of the order of few hours without danger of cell wash out. In addition, high system efficiency can be maintained over a wide range of organic loading rates. The systems are relatively stable and recover from shock loads within few days. They also resist temperature changes better than the suspended growth process. At the same time, gas production rate and removal facilities are better than the high rate suspended growth processes.

2.2.1 Anaerobic Contact Reactor

While a high solids retention time (SRT) is necessary for efficient methane fermentation, a low hydraulic retention time (HRT) is desirable for economic system. The conventional system is not able to separate SRT and HRT and thus larger reactor volumes are required. Anaerobic contact reactor was developed in the early 1950s from the concept of recycling biological solids to obtain a larger retention time as in the activated sludge process (Schroepfer, *et al.*, 1955). Thus, it can be considered as an anaerobic activated sludge process. In this reactor, the microbial flocs settled down in the settling tank are recycled and brought into contact with raw wastewater (*Figure 4*). The performance of this type of reactor depends on the degree of mixing of reactor contents and the settleability of the bacteria. Well settled bacteria will enable good recycling to reactor. The

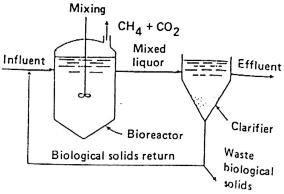


Figure 4. Anaerobic Contact Reactor

problems and limitations of the process are caused by difficulties of control due to:

i) difficulty to provide adequate mixing facility for large reactors.

ii) settling of microorganisms from the reactor liquid.

iii) difficulty in predicting the amount of microorganisms settling in the clarifier.

iv) instability of the process at high methane production rates, causing long term set backs.

Experience with the anaerobic contact process has shown that this process is best suited for the treatment of either concentrated or naturally warm waste. In general the process is found to be not satisfactory for a waste containing less than 2,000 mg/L BOD_5 at temperature less than 30°C. Martensson and Frostell (1982) reported that so far the highest loading rate for the anaerobic contact reactor treating wastewater is from a sugar beet factory. By operating the reactor at the organic loading rates of 12 to 24 g COD/L/d, they obtained a COD removal efficiency of 86 to 89%.

2.2.2 Clarigester

This is a variation of the anaerobic contact reactor in which the settling compartment is located above the reactor (*Figure 5*). Unlike the anaerobic contact reactor, the clarigester has no mechanical mixing. The wastewater enters the reactor through a number of inlets at the base of the reactor and through a rotating pipe and flows upward through a dense bed of bacterial flocs. It has been reported by Callander and Barford (1983), that by working at a loading rate of 3 kg COD/m^3/d, the clarigester was able to remove COD by 97 – 98%.

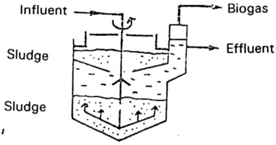


Figure 5. Clarigester

2.2.3 Downflow Stationary Fixed Film (DSFF) Reactor

The downflow stationary fixed film reactor is relatively a recent addition to the family of advanced high rate anaerobic reactors, all of which are based on retention of the active biomass. This type of reactor was developed by the National Research Council in Ottawa (Van den Berg *et al.*, 1980). This reactor distinguishes itself from other types of advanced reactors by the downflow mode of operation, the architecture of its packing (fixed biofilm support), and the absence or near absence of suspended growth.

The downflow mode of operation dictated a stationary film support to maintain the film of microorganisms in the reactor. Additionally, to prevent settling of suspended solids on parts of the film support surface, the stationary film support is arranged in more or less vertical channels and are made of potters clay, draintile clay, needle punched polyester or polyvinyl chloride.

The raw wastewater enters in the upper part of the reactor and flows downward through the fixed packing which contains only an active biomass film. The suspended growth in the reactor is removed by the downward movement of the wastewater. The formation of stable and active biomass film on the surface of packing material is the important factor which determines the efficiency of this reactor (Van den Berg and Kennedy, 1981 and Murray and Van den Berg, 1981). The schematic diagram of this reactor is shown in *Figure 6.*

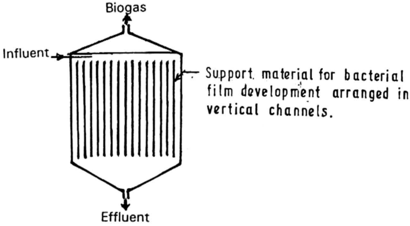


Figure 6. Down-Flow Stationary Fixed Film (DSFF) Reactor

The fixed film reactor has the advantage of greater resistance to wash out of biomass attached to the stationary support whereas the suspended growth biomass is susceptible to wash out by hydraulic shock loading. In this type of reactor, the amount of retained biomass depends on the surface to volume ratio, and therefore limited by the support matrix area. This fixed film reactor with wastewater removal from the bottom has been found to produce methane from wastewaters with high suspended solids content where as in the other reactor design, the suspended particles which are undigestible and/or inorganic in nature may seriously decrease the reactor efficiency by plugging or clogging of the sludge blanket or the filter matrix (Van den Berg,1982).

The DSFF reactor has been applied for many types of wastewater at an organic loading rate ranging from 6 to 25 kg COD/m^3.d which gave a COD removal efficiency of 57 to 75% (Stevens & Van den Berg,1981, Van den Berg & Kennedy , 1981, 1983, Hall et al, 1982 and Szendrey, (1983). The biggest full scale DSFF reactor (13,000 m^3) was reported by Szendrey (1983) for the treatment of rum stillage wastewater in which 65 – 70% of COD was removed at a loading rate of 13 kg COD/m^3.d..

2.2.4 Fluidized and Expanded Bed Reactors

The fluidized and expended bed reactors consist of a bed of fine particles (size 0.2 – 2 mm) such as sand, PVC beads, ion exchange resin, porous alumina, and etc, upon which the biomass grows in thin film (see *Figure 7*) . The upward velocity of the influent and the recycled liquor causes an expansion of the bed, 30 to 100% for the fluidized bed reactor and 10 to 2 0% for the expanded bed reactor (Callander and Barford, 1983). These reactors have much larger surface area per unit reactor volume, which increases the reactor

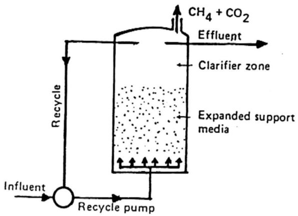


Figure 7. Fluidized and Expanded Bed Reactor

microorganism concentration. A specific surface area of 3,000 m^2/m^3 has been reported for fluidized bed reactor (Boening and Larson, 1982).

In the fluidized bed, the particles are in free motion, while in the expanded bed, they remain in stationary contact (Cooper and Wheeldon, 1980). Both reactors can achieve biomass density of 30 - 40 g VSS/L (Switzenbaum, 1978). The fluidized and expanded bed reactors have been applied for treatment of many types of wastewater (Bell *et al.*, 1980; Switzzenbaum, 1982; Morris and Jewell, 1981; Jewell *et al.*, 1981; Li *et al.*, 1982 and Heijnen, 1984). The highest COD removal (80 - 90%) was reported by Li *et al.*, (1982) for the treatment of whey permeate at a loading rate of 8 - 24 g COD /L/d.

2.2.5 Upflow Anaerobic Sludge Blanket Reactor

The upflow anaerobic sludge blanket (UASB) reactor operates entirely as a suspended growth system and consequently utilizes no packing material. It is basically a dense blanket of granular or flocculated sludge placed in a reactor, which is designed to allow the upward movement of wastewater through the blanket. This type of anaerobic reactor (*Figure 8*) was first developed by the Dutch researchers in the 1970s (Lettinga and van Velsen, 1974). Its concept is similar to the up-flow sludge blanket (USB) processes reported by Cillie *et al.*(1969), except that it has been equipped with a proper Gas Solids Separator (GSS) at the upper part of the reactor (Lettinga et al, 1979).

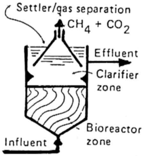


Figure 8. Upflow Anaerobic Sludge Blanket (UASB) Reactor

The main functions of the GSS are:

- to separate the biogas from the mixed liquor and from floating sludge particles.

- to separate the sludge particles or flocs by settling, flocculation and entrapment in a sludge blanket.
- To enable the separated sludge to slide back to the reactor compartment and also to restrict an excessive expansion of the sludge blanket.

The UASB reactor depends on the development of highly settleable biomass either as flocs or as dense granules of 1 – 4 mm size which is achieved through a carefully controlled initial start-up procedure. As a guideline, Lettinga *et al.*(1983) suggested that the amount of seed sludge (digested sewage sludge, digested manure, *etc.*) required is about 10 – 20 kg VSS/ m^3 with the initial sludge loading rate of 0.05 – 0.10 kg COD/kg VSS/d . The undesirable low density of seed sludge components are allowed to be washed out of the reactor while the active biomass with better settling properties is retained in the reactor. A dense bed of granular sludge usually develops at the bottom of the reactor with biomass concentration in the order of 60 kg TS/m^3 (Lettinga *et al.*, 1980).

The UASB reactor has been widely used for treatment of many types of wastewater in the Netherlands, Belgium, Brazil, Cuba, USA and other countries (Van den Berg and Kennedy, 1983). It is normally applied at loading rates between 15 – 30 kg COD/ m^3/d and at 30°C

(Lettinga *et al.*,1983). The highest loading rate of 20 – 30 kg COD/m^3/d which yields a COD removal of 88 – 94% was reported by Van den Berg *et al.*(1981).

2.2.6 Upflow Anaerobic Filter

The upflow anaerobic filter (*Figure 9*) was first developed by Young and McCarty (1967) using a concept of biofiltration already used in the aerobic trickling filter of sewage treatment plants. This reactor is typically operated in an upflow mode to ensure the fixed packing is in submerged condition in order to maintain the anaerobic conditions. Since this type of anaerobic reactor is used in the present study, it is further described in detail in *Section 2.4*.

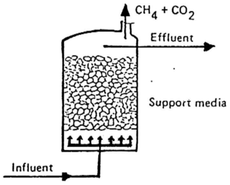


Figure 9. Upflow Anaerobic Filter

2.3 Factors Controlling the Anaerobic Digestion Process

As the anaerobic digestion is a biological process, its performance in wastewater treatment will certainly be affected by the factors which influence the growth of microorganisms involved. Such factors include the nutrients, pH, redox potential, temperature, and the presence of toxic substances.

2.3.1 C: N Ratio

The microorganisms involved in the anaerobic digestion process require carbon, nitrogen, phosphorus, and other nutrients such as sodium, potassium, calcium, magnesium, iron, sulphur, etc. in trace quantities in order to grow and multiply. The optimum ratio of carbon to nitrogen is between 20:1 and 30:1 (Hawkes, 1979). Since the carbon content of wastewater is normally characterized by the COD, the C/N ratio is also expressed in terms of COD. The optimum COD/N ratio is about 100:1.25 and COD/P ratio is in the order of 100:0.25 (Verstraete, 1984).

2.3.2 pH

The pH is one of the important factors which influences the anaerobic digestion process. McCarty (1964) reported that the optimum pH for the anaerobic digestion process is between 7.0 and 7.2. He also found that the methane producing bacteria (MPB) and the acid producing bacteria (APB) are inhibited when the pH drops to 6.6 and 4.5

respectively. According to Kugelman and Chin (1971), under balanced digestion conditions, the biochemical reactions tend to maintain automatically the pH around neutral. Although volatile fatty acids produced by the APB tend to reduce the pH, this effect is counteracted by the breakdown of these acids by the MPB and also by the reformation of bicarbonate buffer during methane digestion. However, if an imbalance develops, the APB outpaces the MPB and volatile fatty acids build up in the digester. This results in a drop in pH which stops methane production almost completely but hinders acid formation only slightly. Normally, when this happens, a small amount of base such as lime or soda ash is added to the digester to bring back the pH to neutral range (Verstraete *et al.,* 1981).

2.3.3 Redox Potential

The MPB unlike the APB are strict anaerobes, since a low concentration of dissolved oxygen proved detrimental to these bacteria. Thus, it is essential that a highly reduced environment be maintained to promote their growth (Pfeffer, 1979). The optimum methane production was reported by Dirasian *et al.*(1963) to occur at redox potential between –520 and –530 mV.

2.3.4 Temperature

The anaerobic digestion process can be carried out satisfactorily at two temperature ranges, namely mesophilic (optimum: 35 – 40° C) and thermophilic (optimum: 55 - 60 ° C) (Pfeffer, 1979). It has been reported that the rate of anaerobic digestion is higher at high temperatures (Fair and Moore, 1937; Maly and Fadrus,1973; Pfeffer, 1974; Zeikus, 1979). According to Zeikus (1979), the thermophilic bacteria have limited species composition and are able to grow well at the thermophilic temperature due to the presence of thermostable macromolecules.

2.3.5 Volatile acids, irons, heavy metal and other chemicals

High concentration of volatile acids, cations (Na^+, NH_4^+, K^+, Ca^{2+}, *etc.)*, heavy metal ions (Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, *etc.)*, aromatic compounds (chloroform, phenol, p-cresol, DDT,*etc.)*,free ammonia and sulphide are toxic to anaerobic microorganisms especially the MPB.

Earlier studies by Buswell (1947), Schlenz (1947), Schulze and Raju (1958) and Mueller *et al.*(1959) showed that volatile acids produced by the APB are toxic to MPB at concentrations above 2,000 mg/L. The inhibition of methanogenesis due to volatile acids is signaled by a drop in the pH. According to Buswell (1947) and Schlenz (1947), the addition of alkaline substances to bring back the pH to the neutral range could not overcome the toxicity effect of volatile acids because the volatile acids are only toxic to MPB and not to APB. Thus, the addition of alkaline substances only stimulate the production of volatile acids leading to even greater toxicity. These authors suggested that the inhibitory effect of volatile acids could be overcome by reducing the loading rate and by diluting the reactor contents. However, it was later reported by Kugelman and Chin (1971) that volatile acids are not toxic to MPB at concentrations up to 6,000 mg/L. At this level, propionic acid is slightly toxic to APB. Thus, they concluded that the pH control with alkaline substances is a valid procedure to overcome the inhibitory effect of volatile acids on methanogenesis.

The effect of cations such as Na^+, K^+, NH_4^+, etc. is always referred to as "salt toxicity" on methanogenesis (McCarty and McKinney, 1963). High salt levels cause the bacterial cells to dehydrate because of osmotic pressure (De Baere *et al.*,1984). Although the cations of salt in solution must always be associated with the anions, the toxic action of salts was found to be predominantly determined by the cations (McCarty and McKinney,1963). Kugelman and McCarty (1965) found that sodium ion concentrations of 3.5 to 5.5 g/L caused a moderate inhibition, while the concentrations of more than 8 g/L strongly inhibited the methanogenesis. Based on the equivalent concentration, McCarty and McKinney (1963) observed the following order of increasing toxicity of cations on MPB: calcium, magnesium, sodium, potassium and ammonium. They also noticed that the ammonium ion toxicity appeared similar in nature to the toxicity of other ions at low pH but appeared related to the concentration of free ammonia in solution at high pH. According to McCarty (1964), total ammonia-nitrogen (Free NH_3 + NH_4^+) at concentrations of more than 3 g/L inhibited methanogenesis at all pH ranges. De Baere *et al.*(1984) reported that shock treatments with NaCl and NH_4Cl caused a 50% inhibition of methanogenesis at levels of 35 g/L. A complete recovery of methane production occurred after 3 to 5 days and 24 hours for anaerobic reactors receiving a shock dosage of NaCl and NH_4Cl respectively. According to the latter authors, the MPB attached to polyurethane carrier in well functioning flow through reactor can adapt to the increasing amount of salt. They noticed that a 50% inhibition only occurred at 95 and 45 g/L of NaCl and NH_4Cl respectively.

Free heavy metal ions such as Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Fe^{3+}, Ag^+, etc, have been reported to have a toxic effect on the anaerobic microorganisms (Mosey and Hughes, 1975). A method to predict the effect of a mixture of heavy metal ions on the anaerobic digestion process has been proposed by Mosey (1976). According to him, inhibition on anaerobic digestion can be expected when

$$\frac{Zn/32.7 + Ni/29.4 + Pb/103.6 + Cd/47.4}{\text{solids concentration}} > 400 \text{ meq/kg} .$$

In this case, the concentrations of heavy metals Zn, Ni, Pb and Cd are in mg/L and solids concentration is in kg/L. Matsumoto and Noike (1979) have reported the effect of different heavy metals (Cu, Zn, Ni, Cd and Cr) separately at a concentration of 3,000 mg/L and as a mixture at a concentration of 200 – 400 mg/L each on anaerobic digestion of sludge. They found that all metals resulted in irreversible inhibition, except Cr which exhibited initial inhibition, followed by rapid recovery. Activities of both APB and MPB, were inhibited. According to these authors, the inhibition by combined metals was more pronounced at lower total metal concentration than for each metal separately.

Lingle and Herman (1975) observed that the presence of 2200 mg/L of mercury caused significant inhibition on the anaerobic digestion process. Since the toxicity of heavy metals is related to free ions, the degree of toxicity depends among other things on the presence of complexing or precipitating anions. In this respect the presence or formation of sulphide is particularly important because most heavy metal sulphides are extremely insoluble (no longer toxic). The relationship between sulphide concentration and the degree of inhibition of anaerobic digestion by heavy metals was investigated by Mosey and Hughes (1975). They determined the pS (- log S^{2-}) from mV reading measured by a Ag/AgS electrode. According to them a pS value greater than 14 in the digesting sludge indicated the presence of inhibitory concentration of Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+} or Cu^{2+}.

The effect of toxic organic compounds on the anaerobic digestion process has been studied extensively as a result of increasing interest in the use of anaerobic digestion process in the treatment of industrial wastewaters, which usually contain these compounds. Swanwick and Foulkes (1971) studied the inhibitory effects of chlorinated hydrocarbons on the anaerobic digestion of sewage sludge. In this study they used batch digesters of 440 mL capacity in which raw sludge and actively digesting sludge together with test compounds were added. The inhibition was shown by a drop in gas production compared with that of a control. They found that chloroform is extremely toxic to the anaerobic digestion of sewage sludge (50% inhibition at a chloroform concentration of about 25 mg/kg dry sludge or 0.0025%) and 1,1,1-trichloroethane is equally toxic at higher concentration, but less so at lower concentrations. Chlorobenzene, orthochlorobenzene, parachlorobenzene and certichlor were less toxic and the concentrations to give a 50 % inhibition were respectively 2.1, 2.4, 3.0 and 2.5 % (w/w). According to these authors, solids content, proportion of undigested solids in a digester, level of bacterial activity and presence of other toxicants are important factors influencing the inhibitory effect of these compounds.

Stuckey *et al.*(1980) evaluated the effect of four organic compounds namely methylene chloride (MC), vinyl chloride (VC), vinyl acetate (VA) and ethylene dichloride (EDC) on the anaerobic digestion process using batch and semi-continuous digesters. The concentrations to give a 50% inhibition were 14, 40, 1150 and 50 mg/L for MC, VC, VA and EDC respectively. They also found that the degree of toxicity depends on the degradability and volatility of the compounds and the ability of the microorganisms to acclimate to these compounds.

Using batch assay techniques, Johnson and Young (1983) examined the effects of organic compounds on the anaerobic digestion process. Of these, only six compounds (nitrobenzene, 4-nitrophenol, 2-nitrophenol, hexachloroethane, 2,4-dichlorophenol and hexachloropentadiene) were found to exhibit significant inhibitory effect (> 50% reduction in biogas production). They found that the recovery of the inhibitory effect is due to the degradation of the compounds to less or non-toxic compounds. As an example, nitrobenzene (toxic) is degraded to aniline (non-toxic) ie. a reduction of nitro group to amino group.

These authors suggested that the relationship between hydraulic retention time (HRT) and solid retention time (SRT) is also an important factor in establishing the inhibitory effect of toxic organic compounds. When the HRT decreases relative to SRT (eg. in anaerobic filter, fluidized bed reactor, UASB, etc.), the inhibitory effect of the compounds should be lower because the contact between biological solids and organic compounds is shortened.

Out of 94 organic compounds tested, Shelton and Tiedje (1984) found that the following compounds namely 5-chlorosalicyclic acid, p-nitrophenol, m-chlorophenol, p-chlorophenol, chloroform and hexachloropentadiene, trichloroacetate acid, 4-phenoxy butyric acid and atrazine are toxic to the anaerobic digestion process. Van de Ven (1984) investigated the effect of shock dosage of 0 – 10 mg/L of 10 compounds which is normally present in the pharmaceutical wastewaters on the anaerobic digestion process. He found that six products show strong toxicity effects, These products are allylchloride (0.87 g/L), emidazol (0.75 g/L), isopropanol (0.75 g/L), formic acid (0.4 g/L), tetrahydrofuran (4.7 g/L) and toluene (0.53 g/L). Figures in bracket indicate the minimum levels which are toxic to the anaerobic digestion process.

The toxic effect of the organic compounds in the anaerobic digestion process could be overcome by removing the organic compound from the wastewater prior to digestion. Swanwick and Foulkes (1971) suggested that most of the organic compounds could be removed by air-stripping since they are normally volatile. They found that, in order to reduce the chloroform level in a sewage sludge from 5 mg/L to 0.3 mg/L, a level which is no more toxic to the anaerobic digestion process, the sludge has to be aerated for 3 hrs using 34 volumes of air per volume of sludge.

Sulphide is required by the anaerobic microorganisms as a sulphur source for their normal growth. The optimal sulphide level for the growth of MPB is in the order of 1 - 25 mg/L (Speece, 1983). However at a slightly higher level, sulphide is also toxic to the same organism. According to Speece and Parkin (1983), the methane production from unacclimatized batch digester was inhibited by a sulphide level of 50 mg/L. Sulphide was normally produced from the microbial reduction of sulphate present in the wastewater.

2.4 Upflow Anaerobic Filter

The principle of operation of an upflow anaerobic filter is that the wastewater is passed through at low velocities through a column filled with packing material. The packing material acts as a surface for the attachment of microorganisms and as an entrapment mechanism for unattached microorganisms. The attached and entrapped anaerobic biomass will convert both soluble and particulate organic matter in the influent wastewater tó methane and carbon dioxide as the wastewater flows upward through the column. The actual contribution of attached biomass and suspended biomass had been studied by Subramanyam and Sastry (1989a) in an upflow anaerobic filter treating tapioca starch wastewater. They found that the attached biomass and the suspended biomass contributed to about 76% and 24% respectively to the COD removal.

The essential features of the upflow anaerobic filter design are:

i) A distributor in the bottom of the column.

ii) A media support structure.

iii) An inert packing material.

iv) A free board above the packing material

v) Effluent draw off.

vi) Operational features such as recycling facilities or a sedimentation zone below the packing material.

The distributor is designed for the even distribution of the incoming wastewater stream, over the packing whole cross-sectional area of the anaerobic filter column to avoid short-circuiting. The free board above the packing material is designed as a head space to allow for the accumulation and capture of biogas. Various provisions are made for the draw-off and utilization of the biogas, which consists mainly of methane and carbon dioxide, with smaller amount of hydrogen sulphide, hydrogen and other trace gases.

Recycling of effluent back to the influent is not usually practised in the operation of the anaerobic filter. Anaerobic filters are generally designed as one-pass-plug flow reactors, taking advantage of the high driving force of the undiluted incoming wastewater stream.

Two of the major design parameters for the design of anaerobic filter are the hydraulic retention time (HRT) and the organic loading rate. The value of these parameters will depend upon the influent wastewater characteristics, temperature, and the desired efficiency of removal or rate of biogas production. As far as possible these design parameters should be based on experience obtained with full scale experiments (Switzenbaum, 1982). Laboratory and pilot scale anaerobic filters have been operated at HRT values of three to several hundred hours and at organic loading rates of 0.4 to 50 kg COD/m^3/d (Henz and Harremoes, 1982; Subramanyam and Sastry, 1988a,1988b). Full scale industrial applications employ HRT values in the range of 1 to 10 days and organic loading rates from 4 to 16 kg COD/m^3/d (Switzembaum, 1983). Hydraulic Retention Time (HRT) is calculated on the basis of liquid volume of the filter (or void volume). HRT is the ratio between the void volume and the influent flow rate of the wastewater.

Data collected by Young (1968) and Young and McCarty (1968) indicated that a linear relationship existed between COD removal efficiency and the inverse of the HRT in the voids within the rock-filled anaerobic filters. This can be represented by the following equation:

$$E = 100(1 - k/\mathrm{HRT})$$

Where E = COD removal efficiency (%),

HRT = hydraulic retention time, and

k = a proportional coefficient.

The COD removal data for the investigations carried out by Young and Dahab (1982) followed a similar trend but had a different value for each media type and size. The above equation provides only an empirical description of COD removal in the anaerobic filter. For the data of the four media studied by Young and Dahab (1982), plus the rock media by Young (1968), it was suggested that the relationship is fairly dependable. One objective of the pilot tests would be to determine the value of k for specific types of media proposed for use in full-scale anaerobic filters.

Raman and Khan (1982), in their study of anaerobic filter treating raw sewage obtained about 80% BOD_5 and about 89% suspended solids reduction at HRT of 6 to 8 hours. Suthakar (1981) reported that an HRT of one day is an optimal condition in treating septic tank effluent and it can reduce 62% total COD and 49% suspended solids.

2.4.1 Packing Material

A wide variety of materials of different sizes have been used in anaerobic filter studies. In general the material selected should have a high specific surface (surface area to volume ratio) to provide a large surface for attached biofilms, while maintaining a sufficient void volume to prevent the reactor from plugging either from particulate solids entering with the influent wastewater stream or bacterial floc growth within the reactor. Since the upflow anaerobic filter consists of both attached and suspended biomass (Subramanyam and Sastry, 1989a), the choice of packing material is quite important (Switzenbaum, 1983). Quartzite stones and plastics are normally used as the packing material in the upflow anaerobic filter (Richter and Mackie, 1972; Van den Berg and Lentz, 1979; Young and Dahab, 1982 and Subramanyam and Sastry, 1989a,1989b). Other materials such as polyurethane foams and rubberised coir have also been tried as packing media for the upflow anaerobic filter (Poels *et al.*,1984; Zaid, 1988a,1988b, 1990,1991a, 1994).

2.4.2 Start-up Process

It has been reported by Young and McCarty (1967) that the start-up of the upflow anaerobic would take between 0.3 to 1.3 months and that the filters seeded with sludge from identical processes have started four times faster than the ones seeded with municipal sewage sludge. Salkinoja-Salomen *et al.*(1983) observed that temperatures around 35°C, porous surface of packing material, presence of carbohydrates in the wastewaters and addition of slime producing organisms increased the start-up rate. They felt that the period taken to attain steady state has to be considered as the start-up period, as only then there will be sufficient biomass in the filter. Reactors with acclimatized seed needs less start-up time.

Lovan and Foree (1972) reported that the addition of trace elements had no effect on the start-up of the anaerobic filter. According to Van den Berg and Kennedy (1983), the start-up of anaerobic filter is faster with diluted wastes and that the associated bacteria secreted *Glycocalyx* which helped in the deposition of the biomass. The initial deposition of the methanogenic bacteria is necessary for a good start-up process.

2.4.3 Industrial Application

During the last three decades many investigations have been carried out with a wide variety of industrial wastewaters using upflow anaerobic contact filters . The tendency has been to try to treat increasingly more difficult wastewaters. A summary of several anaerobic filter studies for a variety of wastewaters is given in *Table 4.*

2.4.4 Operational Problems

It has been reported that there may be some operational problems associated with the upflow anaerobic filters. These problems are:

i). Channeling and Short Circuiting

In anaerobic filters, gas bubbles may adhere to flocs/bed particles and cause these to rise in the reactor, and may result in washout of biomass or deterioration of the effluent quality. Gas bubbles entrapped in filters may cause channeling and short-circuiting in the reactor (Henz and Harremoes, 1982).

Table 4. Upflow Anaerobic Filter Studies for Industrial Wastewaters

Wastewater	Inf.COD mg/L	Eff. COD mg/L	Removal %	Loading Kg COD/m³.d	HRT d	Reference
Fish processing	466	90	81	-	3.1	Hudson *et al.* (1978)
Potato processing	3,000	-	41-79	-	0.5-2.5	Pailthrop *et al.* (1971)
Whey	8,100	-	-	1.9	-	Hakannson, 1972 (Quoted by Switzenaum, 1982)
Whey permeate	5,000	-	-	0.7	-	Hakannson, 1972 (Quoted by Switzenaum, 1982)
Pharmaceutical waste	2,000	-	70-80	-	36	Jennett and Rand, 1981 (Quoted by Switzenaum, 1982)
Tapioca starch waste	4,000	1,115	72	16	6h	Subramanyam and Sastry (1989a)
Perfumery Wastewater	2,100	638	69	8.4	6h	Subramanyam and Sastry (1988b)
Distillery Wastewater	50,000	26,250	48	50	1	Subramanyam and Sastry (1989b)
Phenolic wastewater	2,500	2,065	17	5	0.5	Subramanyam and Sastry (1990)
Sago mill Wastewater	4,000	1,115	72	16	6	Subramanyam and Sastry (1988a)

ii). Filter Clogging

Due to clogging only part of the retained sludge will effectively contact the wastewater, as a result the contact time between the sludge and the wastewater will be relatively short. In full scale studies (Raman and Chakladar, 1972; Khan and Siddique, 1976; Raman and Khan,1977; Raman and Khan, 1978), filter clogging has been reported after 18 months of continuous operation. Wasting of sludge from the filter can be accomplished by flushing water from the top through an idle filter and removing the solids (Raman and Chakladar, 1972).

2.5 Treatment of Wastewater from the Rubber Products Manufacturing Industry

There were about 135 rubber products manufacturing factories actively operating in Peninsular Malaysia in 1992 (Zaid, 1992b). Of these, a total of 35 factories (about 26%) had put up suitable systems for treatment of their wastewaters (see *Table 5*). The systems adopted include the flocculation and activated sludge, flocculation, anaerobic digestion and aerated lagoons, flocculation and aerated lagoons, anaerobic/facultative ponding and flocculation together with sand filtration (see *Table 6*).

Table 5. Treatment of Wastewater from Rubber Products Manufacturing Industry in Malaysia (Zaid,1992b)

Product	No. of Factories in Operation	No. of Factories with Wastewater Treatment Plants
Rubber gloves	87	20
Rubber thread	5	3
Catheters	5	0
Condom	3	0
Swim caps	1	0
Balloons	3	0
Rubber toys	2	0
Finger cots	1	0
Foam products	5	1
Teats and soothers	1	0
Mixed products	22	11
TOTAL	135	35

In most of systems, different types of chemical flocculants are used to remove zinc and other metallic elements from the wastewaters. Examples of these chemical flocculants/precipitants are sodium sulphide, lime, magnafloc, kemfloc, aquafloc, koagen, etc. The effectiveness of these flocculants in removing zinc and other metallic elements were found to vary from factory to factory depending on the

Table 6. Types of Wastewater Treatment Systems Adopted by the Rubber Products Manufacturing Industry in Malaysia (Zaid, 1992b)

Types of Wastewater Treatment Systems	No. of Factories Adopted	% Total
Flocculation & Activated Sludge	25	71
Flocculation, Anaerobic Digestion & Aerated Lagoon	2	6
Flocculation & Aerated Lagoon	1	3
Anaerobic/Facultative Ponding	5	14
Flocculation & Sand Filtration	2	6
TOTAL	35	100

types of flocculants used, their application dosage and the characteristics of the wastewaters. It was reported by Zaid (1991) that by using lime alone as a flocculant, one of the rubber thread manufacturing factories was able to remove zinc from the wastewater by about 90%. The final discharge however still contained about 30 mg/L of zinc which is far above the permissible limit of 1mg/L.

The flocculation and activated sludge is the most common wastewater treatment system used by the rubber products manufacturing industry in Malaysia. In this system (*see Figure 10)*, the

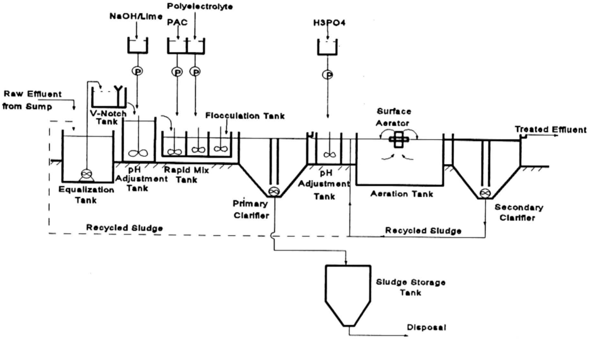


Figure 10. Schematic Diagram of the Flocculation and Activated Sludge System

wastewater is first subjected to a pH adjustment by adding lime or caustic soda solution before it is flocculated with suitable flocculants for the removal of zinc and other metallic elements. The flocculated material is then removed through a primary clarifier. The clarified liquor is further treated in an aeration tank (activated sludge) for the removal of other pollutants such as BOD, COD, nitrogen, etc.

Since the activated sludge process performs best at neutral pH, phosphoric acid is normally added to the clarified liquor before it flows into the aeration tank. Phosphoric acid is used to neutralize the pH because it also increases the level of phosphate required by the aerobic bacteria which are responsible for the process. In order to maintain the required COD/N/P ratio for these bacteria, urea (N source) is also added to the wastewater in the aeration tank. Before discharging the treated wastewater to river, the wastewater has to pass through a secondary clarifier for the settling of sludge. Zaid and Nordin (1991) reported that the flocculation and activated sludge system was found to be effective for treatment of wastewater from rubber glove manufacturing factories. They found that the COD, BOD and zinc removal efficiencies obtained from the monitoring of five factories using the system ranged from 48-93%, 44-97% and 20-58% respectively.

The flocculation, anaerobic digestion and aerated lagoon system is adopted by two of the rubber thread manufacturing factories. In this system, sodium sulphide and polyelectrolyte are used in the flocculation unit for the removal of zinc. After the primary clarifier, the clarified wastewater is further treated in a high rate anaerobic digestion system (upflow anaerobic sludge blanket or UASB reactor) for the removal of COD and BOD. After the anaerobic digestion stage, the treated effluent is then treated in a number of aerated lagoons. Zaid (1997) found that this system was able to remove about 88% of COD, 92% of BOD and 98% of Zinc. The final discharge had complied with the Standard A of the DOE discharge limits for the respective parameters.

The chemical flocculation and anaerobic treatment of rubber thread manufacturing wastewater was also studied by Abdullah (1994). By using alum as a flocculant and an upflow anaerobic filter with PVC rings as the packing media, this author obtained the BOD, COD and zinc removal efficiencies of about 56%, 53% and 99% respectively. He concluded that an aerobic treatment system is still necessary in order for the treated wastewater to comply with the DOE discharge standards.

The flocculation and aerated lagoon system is adopted by one of the rubber thread and a number of rubber glove manufacturing factories. This system however was not that effective for treatment of rubber thread manufacturing wastewater. Zaid (1991) observed that by using this system, one of the rubber thread manufacturing factories was able to achieve the COD, BOD and zinc removal efficiencies of about 10%, 30% and 88% respectively.

The same type of anaerobic/facultative ponding system used by the rubber processing industry is adopted by the rubber products manufacturing industry in Malaysia. This system is also effective in removing the pollutants from the wastewater. It was reported by Zaid (1992b) that by using the above system for treatment of wastewater from a swim caps manufacturing factory, about 84% of COD, 88% of BOD and 50% of zinc were removed. However, since the rubber products manufacturing factories are located in the industrial estates which have land constraint, this system is not widely adopted by this industry.

The flocculation and sand filtration system has been used by two of the rubber gloves manufacturing factories in Malaysia. According to Zaid (1992b), the above system is not effective in treating this type of wastewater. He reported that the average COD, BOD and zinc removal efficiencies obtained were about 47%, 33% and 73% respectively.